Effects of Ionic Liquid Composition on Conductivity of Diblock Copolymer Electrolyte Membranes

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Introduction:

Polymer electrolytes are promising in that their development could spur the creation of batteries through the use of these electrolytes to replace the salts currently used in lithium-ion batteries that require solvation in flammable organic solvents.[1] The possible applications and benefits of improved cells that enable the use of pure metal electrodes or an accessible open option for use in fuel cells is quite clear. With increasingly pervasive numbers of electronic devices used on a daily basis by more people demanding lighter, thinner devices with better battery life provides enough motivation for the development of appropriate polymer electrolytes. Potential application in open systems of such an electrolyte for use in fuel cells is also appealing due to the increasing interest in renewable energy sources. There is clear motivation for pursuing polymers appropriate for such uses.

Inevitably, it is important to analyze what is to be demanded of a polymer electrolyte membrane (PEM) based on the problems currently of concern with such membranes. Lithium metal electrodes are of interest due their ability to improve performance of batteries, but cause an issue when dendrites form on the electrodes upon discharge and recharge cycles.[2] Formation of metal dendritic structures through the electrolyte present a large hazard to the use of lithium-ion battery cells. Their growth, if unhindered, inevitably leads to a dendrite spanning the gap through the electrolyte to the opposite electrode. A short-circuit would result, causing at best the destruction of the battery, possibly causing a fire that would be a risk to the device, the user, and surrounding objects. A previous study has demonstrated that an electrolyte having a shear modulus of 10^9 Pa would prevent dendritic growth, and as such provides a goal for PEM development.[3]

Recent work has created a promising diblock copolymer that, when synthesized with a room-temperature ionic liquid (RTIL) present, is able to exhibit mechanical properties close to those we have just discussed while providing a relatively high conductivity somewhat below the 10^{-3} S cm^{-1} required for a commercially viable battery.[4,5] Working from the success of Schulze et al., investigation into the impact of the identity of the RTIL upon the conductivity of the PEM samples was identified as an area where improvement might be possible. The

RTIL used previously, [1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide] (BMITFSI), was considered for replacement with another similar compound, [1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide] (EMITFSI), where one butyl group has been replaced by an ethyl group. Although this seems like a small change, a smaller-sized ion should improve the conductivity of the PEM samples.

Experimental:

Using the methods detailed by Schulze et al., one-pot synthesis was used to create polymer samples using 28 kg/mol PEO with a chain-transfer agent, styrene and divinylbenzene monomer in a 4:1 ratio, a radical initiator, and EMITFSI.[5] Conductivity was calculated from measuring the bulk impedance between 30 and 150 °C.

Results and Discussion:

Measurements were made on two samples, one with 12 vol% and the second with 21 vol% RTIL. The Arrhenius plots are recorded below in Figure 1.

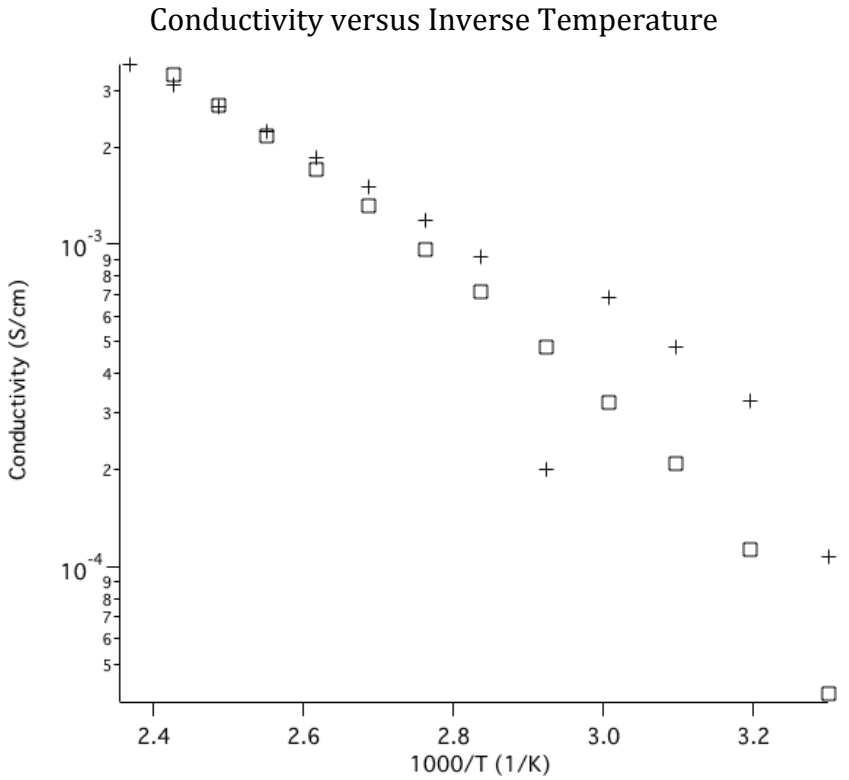

Figure 1: Shows the conductivity of a 12 vol% RTIL polymer sample (+) and 21 vol% (squares).

The two samples with conductivity plots in Figure 1 were measured under the same conditions as one another and those containing BMITFSI reported by Schulze et al. Based on comparison to the conductivity plots recorded there, the

12 vol% samples qualitatively possess the same trend as would be expected for a 12 vol% sample containing BMITFSI instead of the EMITFSI that was used. The 21 vol% sample, in Figure 1 as squares, has a much lower value for conductivity than would be expected, even if no difference was observed based on the RTIL identity.

With only two sample measured, it is difficult to draw any reliable, broad conclusions. Testing of additional samples is required to provide a meaningful comparison to the BMITFSI sample data already reported. As it stands, the data indicate a lack of initial support for the idea that the conductivity of samples can be increased by altering the RTIL through a small change in the size of one alkyl chain in the RTIL.

Conclusions:

Initial conductivity measurements for a candidate PEM have been presented using EMITFSI instead of the BMITFSI that was previously detailed. Instead of increasing the conductivity of the PEM as expected, the substitution of EMITFSI for BMITFSI caused the conductivity to either remain close to where it had been or decrease substantially. Further testing on a larger range of concentrations of RTIL is necessary to determine if this is indeed part of a larger trend.

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References:

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